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European Patent Application EP 1 065 230 A2

**Heat-Resistant, Color-Neutral, Antimony-Free Polyesters
and a Method for their Production**

Your Ref: 072403-01

For: Eastman Chemical Company

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 065 230 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Publication date:

3 January 2001 Patent Gazette 2001/01

(51) Int Cl.⁷: C08G 63/82, C08G 63/85,
C08G 63/87, C08G 63/20,
C08G 63/60

(21) Application number: 00121946.8

(22) Filing Date: 17 August 1995

(84) Designated contracting states:

AT BE CH DE ES FR GB IT LI LU NL PT

(30) Priority: 29 August 1994 DE 4430634

(62) Document number(s) of the previous
application(s) according to Art. 76 EPC:
95112912.1 / 0 699 700

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Comments:

This application was filed on 9 September 2000
as a partial application to the application
mentioned under INID Code 62.

(54) [Title of the Invention]:

Heat-Resistant, Color-Neutral, Antimony-Free Polyesters and
a Method for their Production

(57) [Abstract]: The present invention relates to heat-resistant, color-neutral, antimony-free polyesters, [produced] using a titanium polycondensation catalyst, which are characterized by excellent clarity and color neutrality, and a method for their production, which is very readily reproducible, has a very high polycondensation rate even at very low addition of titanium polycondensation catalyst, and in which a significant reduction in thermal degradation and uncontrolled crosslinking of the formed polyester is obtained.

Description

[0001] The present invention relates to heat-resistant, color-neutral, antimony-free polyesters, produced using a titanium polycondensation catalyst, which are characterized by excellent clarity and color neutrality, and in which a significant reduction in thermal degradation and uncontrolled crosslinking is obtained, as well as to a method for their production that is very readily reproducible and has a very high polycondensation rate even at very low addition of titanium polycondensation catalyst.

[0002] Polyesters have gained very great importance in many areas of application. Saturated polyesters are used on a large scale, in particular, for the production of fiber materials, but also other types of molded articles, for example, beverage bottles. Very high requirements on quality of polyesters are imposed for a trouble-free processability of these polyesters by extrusion methods and for further use of the extruded products, for example, in the textile or beverage industry. It is required, in particular, that the processing and application properties of polyester types for specific processes always be the same within very narrow limits. For processing by extrusion methods, for example, by melt spinning, it is of decisive importance that they always have a uniform molecular weight and an always reproducible molecular weight distribution, are free of gel fractions, and, if possible, have no tendency toward yellowing or thermal degradation. For further processing, no catalyst metals, if possible, should be released from the fiber material during dyeing processes, since these must be removed from the dye plant effluent and disposed of by costly purification operations.

[0003] During disposal or recycling of used polyester products, no difficulty should occur from interfering components either.

[0004] The production of polyesters ordinarily occurs by esterification of aromatic dicarboxylic acids or transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols and subsequent polycondensation until the molecular weight required for the intended use is reached.

[0005] Any transesterification is run in the presence of transesterification catalysts that must be deactivated after the conclusion of transesterification by means of the addition of sequestering agents. Phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives are generally used as sequestering agents.

[0006] After esterification or transesterification, polycondensation to the desired molecular weight occurs, which is also run in the presence of an appropriate catalyst. Antimony compounds, generally antimony trioxide, have gained acceptance in the industry as polycondensation catalysts. It can happen in this context that part of the antimony compound is

reduced to antimony metal by reducing agents, which leads to graying of the polyester.

Insufficient clarity and a non-neutral color tone are the result.

[0007] The relatively high content of antimony compounds in polyesters is also seen as a drawback, since it makes production more costly. There is the additional possibility that antimony compounds will be released during further processing methods, for example, dyeing. The relatively high content of antimony compounds leads to an effect on the spinning process, in addition to the formation of antimony deposits.

[0008] Proposals have therefore already been made to eliminate the drawbacks of the described production method.

[0009] Thus, it is known that the color tone of polyesters can be improved by adding cobalt compounds and/or optical brighteners. It is also known that titanium compounds can be used as polycondensation catalysts, instead of antimony compounds.

[0010] A method for the production of polyesters in which a cobalt compound is added to improve the color tone of the polyester, which, like the transesterification catalyst, must be complexed before the beginning of the polycondensation, is known from various documents, for example, US-A-3,962,189, JP-PS-28006 (1979), JP-PS-123311 (1976), JP-PS-43564 (1979), JP-PS-111985 (1980), or JP-PS-280048 (1989). The amount of sequestering agent used to complex the cobalt additive according to these documents should lie in the range from 0.5 to 7.5 mol per mol of cobalt compound. According to JP-PS-28006, a P/Co ratio of 0.5 to 1.5 is used, in JP-PS-111985 from 0.7 to 3, in JP-PS-280048 from 0.5 to 7.5 (mol/mol).

[0011] This known method has the advantage that all the drawbacks connected with the use of antimony compounds are eliminated and color-neutral and clear polyesters that are suitable for demanding processing methods and applications can actually be produced with it. However, a drawback is that its reproducibility leaves much to be desired. Occasionally, it is not the desired products that are obtained, but disturbances in the polycondensation reaction occur. The required molecular weights are not reached and during lengthening of the polycondensation time that is deemed necessary, yellowing of the polyester and formation of gel fractions occur by means of uncontrolled crosslinking, along with thermal sensitivity of the product, which seriously compromises further processing. The advantages that the method offers are therefore not always realized.

[0012] It has now been found that heat-resistant, color-neutral, antimony-free polyesters can surprisingly be produced in constantly reproducible fashion by

a)

(i) esterification of aromatic dicarboxylic acids with aliphatic diols or
 (ii) transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols in the presence of 20 to 120 ppm, in reference to the catalyst metal, of a transesterification catalyst that is inactivated after conclusion of transesterification by addition of a sequestering agent, and

b) subsequent polycondensation in the presence of a titanium compound as catalyst.

[0013] On conclusion of esterification or transesterification

- 100% of the amount equivalent to the employed transesterification catalyst and
- 90 to 99% of the amount equivalent to the employed cobalt of phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives are added to the esterification or transesterification charge as sequestering agent and then
- 20 to 80 ppm cobalt is added to the charge in the form of a cobalt compound

and polycondensation is run without antimony addition in the presence of 1 to 10 ppm titanium, which is added in the form of a titanium compound.

[0014] Appropriate transesterification catalysts are known from the literature. For example, compounds of metals of groups 1 (for example, Li, Na, K), group 2 (for example, Mg, Ca) and group 7 (for example, Mn), are suitable for the method, especially those having a certain solubility in the transesterification charge, like salts of organic esters. Salts of group 7, especially manganese, with lower aliphatic carboxylic acids, especially acetic acid, are preferred.

[0015] A preferred embodiment of the method therefore consists of running the transesterification in the presence of 20 to 120 ppm manganese (calculated as metal) in the form of a manganese compound, especially manganese acetate.

[0016] The cobalt compound, added to improve the color tone of the polyester according to the invention, is expediently also a salt of cobalt with an organic acid, for example, with acetic acid or adipic acid. The minimum amount of cobalt compound is dependent on the degree of color shift required in the individual case, in order to achieve a neutral color tone. If optical brighteners are additionally used for color correction, the amount of cobalt compound can naturally be reduced. The required amount of cobalt additive, as mentioned above, is generally 50 ppm maximum (calculated as metal), always in reference to the weight of the polyester. 20 to

40 ppm cobalt is preferably added to the charge in the form of a cobalt compound, i.e., an amount of cobalt compound that corresponds to an amount of 20 to 40 ppm free cobalt is added.

[0017] As in the case of the conventional methods, the transesterification catalyst is also inactivated in the method for the production of polyesters according to the invention before the beginning of polycondensation by adding a sequestering agent, because otherwise polycondensation is hampered, i.e., the required high molecular weights of the polyester cannot be reached and the obtained polyester also has increased sensitivity to thermal loading. The cobalt compounds added before the polycondensation are also complexed, in order to improve the thermal stability of the polyester.

[0018] It is now essential for the method that in no case should the entire added amount of cobalt compound be inactivated, but instead 1 to 10% of the added cobalt compound must remain uncomplexed. The amount of sequestering agent is therefore calculated so that the transesterification catalyst is 100% deactivated by complexing, but only 90 to 99% of the cobalt compound is complexed.

[0019] If the sequestering capacity of the sequestering agent is precisely known, one can simply use 90 to 99% of the amount of sequestering agent equivalent to the amount of cobalt. However, it is generally expedient to determine the required amount of sequestering agent by preliminary experiments. For this purpose, some trial charges of the polycondensation charge, all of which have the same composition as a planned main charge, are mixed with about 80 to 120% of the theoretically required amount of sequestering agent and then subjected to polycondensation under the same conditions.

[0020] On conclusion of the polycondensation reaction, the viscosity reached by all charges (i.e., the obtained molecular weight) is determined. The results of such preliminary series of experiments are shown in the figure. The achieved viscosities are plotted in said figure on a coordinate system versus the ratio of sequestering agent to cobalt compound (for example, the P/Co ratio). It is apparent that only low viscosities, i.e., low molecular weights, can be achieved with unduly high P/Co ratio. Below a certain limit of the P/Co ratio, the achieved molecular weights increase. The intersection point between the flat and rising parts of the curve marks the equivalent P/Co ratio. Up to 99% of the amount of sequestering agent so determined is then added to the main charge.

[0021] It is particularly advantageous if 100% of the amount equivalent to the amount of transesterification catalyst and 90 to 99% of the amount equivalent to the employed cobalt of phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives are added after conclusion of esterification or transesterification to the esterification or transesterification charge.

[0022] The expedient of only partially deactivating the added cobalt compound surprisingly leads to a drastic improvement in the reproducibility of the method and a very high rate of polycondensation is obtained even with a very limited addition of titanium polycondensation catalysts, along with a significant reduction of the thermal degradation and uncontrolled crosslinking of the formed polyester with the result that no yellowing and no gel formation occur. In running the reaction, one therefore also gets by with smaller amounts of brightening [or: *fining* - *translator*] additives and reaches trouble-free processability. The obtained polyesters correspond to the highest quality requirements in terms of clarity and color neutrality.

[0023] All compounds known as sequestering agents and deactivators for transesterification catalysts are suitable, in principle, as sequestering agents for the method. Phosphorous-containing compounds, like phosphoric acid, polyphosphoric acid, phosphorous acid and phosphonic acids and their derivatives, have been shown to be particularly suitable. Special examples of phosphoric acid derivative are the "PHM esters". These are mixtures of alkoxyalted alkylhydroxyalkyl-phosphoric acid esters with the formula $O=P(OR^1)_3$, in which the groups R^1 are the same or different alkyl, hydroxyalkyl or alkoxyalted hydroxyalkyl groups, or phosphonic acid esters of the formula $(R^2O)_2-PO-R^3-COOR^4$, in which R^2 , R^3 and R^4 are alkyl groups.

[0024] Titanium compounds are used as polycondensation catalysts in the method. All titanium compounds already described for this purpose are suitable, in principle, especially potassium titanyloxalate or titanium isopropylate.

[0025] It is particularly preferred to run polycondensation without the addition of antimony in the presence of 1 to 10 ppm titanium to an intrinsic viscosity (IV), measured in dichloroacetic acid at 25°C, from 0.4 to 0.9 dL/g, preferably from 0.5 to 0.7 dL/g, and to a carboxyl group concentration from 10 to 50 mmol/kg, preferably 10 to 40 mg/kg, in the melt and then to the desired final viscosity in the solid phase.

[0026] The final viscosity of the polyesters according to the invention should lie in the range from 0.7 to 2.0 dL/g, preferably from 0.7 to 1.5 dL/g, measured under the conditions just mentioned. The polycondensation time and polycondensation temperature are regulated in known fashion, so that the desired final viscosity is reached. Polycondensation is generally run as usual in polyester production, depending on the type of polyester, at a temperature from 260 to 350°C, preferably under an inert gas, for example, under nitrogen, and/or under reduced pressure, which lies in the range from 0.2 to 10 mbar, preferably from 0.5 to 5 mbar.

[0027] To set specific polyester properties, for example, melt viscosity, it can be desired to produce a defined degree of crosslinking. For this purpose, polycondensation is run without the addition of antimony in the presence of 2-8 ppm titanium and in the presence of up to 1000 ppm, preferably 100 to 500 ppm of compounds that furnish crosslinking structural groups (cross-linking agents).

[0028] Compounds that have at least three functional groups capable of ester formation serve as cross-linking agents. Functional groups capable of ester formation include the OH group, the carboxyl group, alkoxycarbonyl, especially lower alkoxycarbonyl, carboxylic acid anhydride group and reactive groups derived from them. Examples of common cross-linking agents are pentaerythritol, trimethylolpropane, trimellitic acid, trimesic acid, pyromellitic acid, etc.

[0029] For further improvement of the color tone of the polyester and to save part of the cobalt, it has also proven to be expedient to run polycondensation without the addition of antimony in the presence of up to 50 ppm, preferably 5 to 25 ppm, of an optical brightener.

[0030] The chemical composition of the polyester is naturally of greatest significance for its properties. For the production of polyesters according to the invention that are suitable for the aforementioned applications, under the aforementioned conditions for the method

80 to 100 mol% of aromatic dicarboxylic acids of the formula HOOC-X-COOH or their lower aliphatic esters

and

0 to 20 mol% of aromatic hydroxycarboxylic acids of the formula $\text{HO-X}^1\text{-COOH}$ or their lower aliphatic esters with diols of the formula HO-Y-OH are esterified or transesterified,

in which

X in reference to the total amount of di- and hydroxycarboxylic acid, denotes more than 80 mol% aromatic groups with 5 to 16, preferably 6 to 12, carbon atoms and a maximum of 20 mol% aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,

X^1 denotes the p-phenylene group,

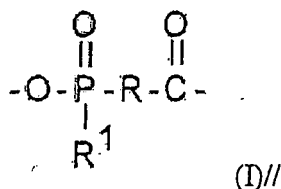
Y in reference to the total amount of transesterified or esterified diols, denotes at least 80 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a maximum of 20 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $(\text{C}_2\text{H}_4\text{-O})_n\text{-C}_2\text{H}_4\text{-}$, in which n is whole number from 1 to 40, in which n = 1 or 2 is preferred for fractions up to 20 mol%, and groups with n = 10 to 40 are preferably only present in fractions of less than 5 mol%.

[0031] It is particularly preferred to choose the starting materials so that

- X in reference to the total amount of di- and hydroxycarboxylic acids, denotes 90 to 100 mol% p-phenylene groups, 0 to 7 mol% m-phenylene groups and 0 to 5 mol% aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and
- X¹ denotes the p-phenylene group,
- Y in reference to the total amount of transesterified or esterified diols, denotes at least 90 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms, or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a maximum of 10 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $-(C_2H_4-O)_n-C_2H_4-$ in which n stands for the numbers 1 or 2.

[0032] It is particularly preferred not to use a hydroxycarboxylic acid of the formula $HO-X^1-COOH$ in the method and to choose the dicarboxylic acid component of the formula $HOOC-X-COOH$, so that X, in reference to the total amount of di- and hydroxycarboxylic acids, denotes 93 to 99 mol%, preferably 95 to 98 mol%, p-phenylene groups, 1 to 7 mol%, preferably 2 to 5 mol%, m-phenylene groups. The aromatic groups, for which X and X¹ stand, can be unsubstituted or, if specific properties of the polyester are to be modified, can carry one or two substituents. The groups are preferably mostly unsubstituted, i.e., no more than 10 mol% of the aromatic groups carry substituents. The precise percentage of substituted groups is established according to the effect to be achieved. The methyl group and sulfonic acid group are preferably considered as substituents.

[0033] In addition to the aforementioned starting materials, up to 10 mol%, preferably up to 7 mol%, other co-condensable compounds can be condensed in the polyester, if specific special properties are desired. For example, poorly flammable polyesters can be produced according to the method, if 1 to 10 mol% of the compounds known from DE-C-23 46 787 and 24 54 189, in reference to the total condensed dicarboxylic acids and optionally hydroxycarboxylic acids, are condensed in the polyester, which yields polyester structural groups of the formula



in which

- R denotes a saturated open-chain or cyclic alkylene, arylene or aralkylene group, preferably alkanediyl with 2 to 6 carbon atoms, cycloalkanediyl with 6 carbon atoms, methylene-phenyl or phenylene, especially ethylene, and
- R¹ denotes an alkyl group with up to 6 carbon atoms or an aryl or aralkyl group, preferably alkyl with 1 to 6 carbon atoms, or aryl or aralkyl with 6 to 7 carbon atoms, especially methyl, ethyl, phenyl or benzyl.

[0034] Up to 10 wt.%, modifying additives, fillers, pigments, dyes, antioxidants, hydrolysis, light and temperature stabilizers and/or processing auxiliaries can be added to the esterification, transesterification or polycondensation charges, if these additives do not inhibit the titanium catalyst. In particular, the addition of up to 10 wt.%, preferably up to 5 wt.%, polyester stabilizers that protect the polyester fraction of the mixture against hydrolysis and thermal degradation is preferred in the method. Those compounds that can react with terminal carboxyl groups of the polyester to nonacid terminal groups, like glycidyl ethers, keteneimines, aziridines, isocyanates, are particularly advantageous as stabilizers. Carbodiimides and polycarbodiimides are particularly advantageous as stabilizers, especially if used in combination with each other.

[0035] The polyesters produced according to the method based on aromatic dicarboxylic acids and aliphatic diols are characterized by the fact that, in the unmatted state, among their color number components

- a* lies in the range from -3 to +3, preferably from -2 to +2,
 b* lies in the range from -6 to +6, preferably -3.5 to +3.5 and
 L* lies in the range from 55 to 75, preferably from 60 to 70.

[0036] The polyesters according to the invention are also characterized by the fact that they are free of antimony and contain

| | |
|---------------|---|
| 1 to 10 ppm | titanium (calculated as metal), |
| 20 to 120 ppm | of a transesterification catalyst metal in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, |
| 0 to 80 ppm | cobalt (calculated as metal), which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives and optionally |
| up to 50 ppm | of an optical brightener. |

The polyester according to the invention is preferably free of antimony and contains

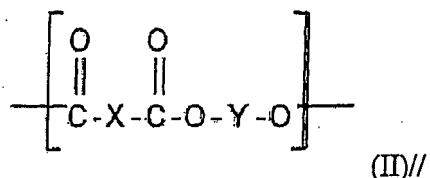
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| 2 to 8 ppm | titanium (calculated as metal), |
| 50 to 90 ppm | manganese (calculated as metal) in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, |
| 20 to 40 ppm | cobalt, which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives and optionally |
| up to 25 ppm | of an optical brightener. |

[0037] It is also preferred that 90 to 99% of the cobalt be present in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives and/or 5 to 25 ppm of an optical brightener be present.

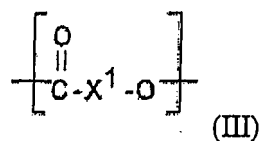
[0038] The catalytically inactive complexes of the transesterification catalyst, preferably manganese, and cobalt, can contain, in principle, all sequestering agents known for inactivation of these metals. Catalytically inactive complexes of the transesterification catalyst are preferred, especially of manganese and cobalt, with phosphoric acid, polyphosphoric acid, or especially phosphorous acid or their derivatives, especially an ester of these acids.

[0039] The structure of the polyester chain is naturally also of special significance for the overall technical features. It can be stated purely qualitatively that it is constructed from the structural groups common in known fiber-forming polyesters. They primarily, i.e., to at least 80 mol%, consist of components that are derived from aromatic dicarboxylic acids and aliphatic diols. Common aromatic dicarboxylic acid components are the divalent groups of benzene-dicarboxylic acids, especially terephthalic acid and isophthalic acid; common diols have 2 to 4 carbon atoms, in which ethylene glycol is particularly suitable. Modified polyesters preferably contain at least 80 mol% ethylene terephthalate units. The remaining 20 mol% is then constructed from dicarboxylic acid units and glycol units that act as so-called modifying agents and permit one skilled in the art to deliberately influence the physical and chemical properties of the products produced from the polyesters, like filaments and packaging materials (for example, beverage bottles). Examples of such dicarboxylic acid units are groups of isophthalic acids or aliphatic dicarboxylic acids, like glutaric acid, adipic acid or sebacic acid. Examples of modifying diol groups are those from long-chained diols, like propanediol or butanediol, di- or triethylene glycol or, if present in limited amounts, polyglycol with a molecular weight of about 500-2000.

[0040] In particular, polyesters, whose polymer chains are constructed from 80 to 100 mol% structural groups of the formula



and 20 to 0 mol% structural groups of formula III



are preferred, in which

- X denotes more than 80 mol% aromatic groups with 5 to 16, preferably 6 to 12, carbon atoms and a maximum of 20 mol% aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,
- X¹ denotes the p-phenylene group,
- Y denotes at least 80 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a maximum of 20 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups with the formula $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$, in which n is whole number from 1 to 40, in which n = 1 or 2 is preferred for fractions up to 20 mol%, and groups with n = 10 to 40 are preferably only present in fractions of less than 5 mol%.

[0041] Polyesters are particularly preferred that consist of structural groups of formula II, in which

- X denotes up to 90 to 100 mol% p-phenylene groups, up to 0 to 7 mol% m-phenylene groups and up to 0 to 5 mol% aliphatic groups of 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and
- Y denotes at least 90 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a

maximum of 10 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups with the formula $-(C_2H_4-O)_n-C_2H_4-$, in which n stands for the numbers 1 or 2.

[0042] In particular, those polyesters consisting of structural groups of formula II, in which X denotes up to 93 to 99 mol% p-phenylene groups and up to 1 to 7 mol% m-phenylene groups are preferred.

[0043] It is often expedient to adjust a defined degree of crosslinking of the polyester. In these cases, it is preferred that the polyesters contain up to 1000 ppm of the aforementioned crosslinking structural groups.

[0044] The polyesters produced by melt polycondensation expediently have an intrinsic viscosity from 0.600 to 0.900, measured in dichloroacetic acid at 25°C.

[0045] Polyesters having structural groups of formula III preferably contain 70 to 100 mol%, especially 85 to 100 mol%, structural groups of formula II and 0 to 30 mol%, especially 0 to 15 mol%, structural groups of formula III.

[0046] The aromatic groups, for which X stands, can all be the same or different in the context of the given definition. In particular, the aforementioned structural groups represented by X, which form the polyester chain to at least 80 mol%,

[0047] can be present individually or mixed in the polyester chain. It is preferred if at least 80% of the polyester chain is formed from only one or two individuals from the groups mentioned for these main components. Any desired additional modification of the polyester chain then preferably occurs by other structural groups in the context of the definition that was given for the structural groups represented by X that are present to a maximum of 20 mol%.

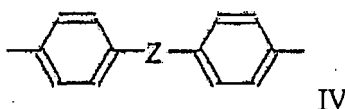
[0048] Thus, the at least 80 wt.% aromatic groups can all be 1,4-phenylene groups or they can consist of 1,4- and 1,3-phenylene groups in a molar ratio from 95:5 to 99:1 or of 2,6-naphthylene groups and biphenyl-4,4'-diyl groups in a molar ratio from 4:6 to 6:4. Polyesters, in which X denotes at least 95 mol% aromatic and a maximum of 5 mol% aliphatic groups, but especially those in which X exclusively stands for aromatic groups, are preferred.

[0049] The groups, for which Y stands, can also all be the same or different in the given definition. In particular, the aforementioned structural groups represented by Y, which form at least 80 mol% of the polyester chain, can be present individually or mixed in the polyester chain. It is preferred if at least 80 mol% of the polyester chain is formed by only one or two individuals from the groups mentioned for these main components.

[0050] Any desired additional modifications of the polyester chain then preferably occurs by other structural groups in the context of the definition given for the structural groups represented by Y that are present to a maximum of 20 mol%. They can be at least 80 wt.% aliphatic groups,

for example, all ethylene groups, or can consist of ethylene and 1,4-dimethylenecyclohexane groups in a molar ratio from 10:1 to 1:10. Polyesters, in which Y is at least 95 mol% ethylene groups, are particularly preferred.

[0051] Preferred aromatic groups, for which X stands, are 1,4- and 1,3-phenylene. Appropriate groups, however, are also 1,4-, 1,5-, 1,8-, 2,6- and 2,7-naphthylene, 4,4'-biphenylene, furylene and groups of the formula IV



in which Z denotes polymethylene or alkylene with 1 to 4 carbon atoms, $-\text{SO}_2-$, $-\text{COO}-$, $-\text{O}-$ or $-\text{S}-$.

[0052] The aromatic groups, for which X stands, can, in turn, carry one or two additional substituents. However, in this case, it is preferred that only a fraction of up to 15%, especially up to 7%, of the present aromatic groups be substituted. The substituted aromatic groups preferably carry only one substituent each. Particularly preferred substituents are alkyl with 1 to 4 carbon atoms, alkoxy with 1 to 4 carbon atoms, chlorine and the sulfo group.

[0053] Groups that are derived from aliphatic dicarboxylic acids and aromatic groups that furnish angled chains, for example, isophthalic acid groups, or which have bulkier aromatic cores, like the naphthalene core, as well as the long-chain structural groups standing for Y, are incorporated in the polyester chain, in particular, if modification of the properties of the polyester is desired. Polyesters that contain less than 7% of these modifying components are preferred.

[0054] To achieve special use properties, incorporation of components containing sulfo groups (for example, sulfoisophthalic acid) in the polyester is used, which acquires an affinity to basic dyes on this account, or the incorporation of structural groups of the aforementioned formula I is used, which leads to poorly flammable polyesters.

Example 1a

[0055] 9.75 kg of dimethyl terephthalate, 0.25 kg of dimethyl isophthalate, 6 kg of ethylene glycol and 3 g of manganese acetate $\cdot 4 \text{H}_2\text{O}$ (68 ppm manganese, in reference to polyester) are fed into an esterification reactor and the mixture is heated during agitation under nitrogen as a protective gas to 140°C . The reaction temperature is raised to 230°C over 4 hours and the split-off methanol and ethylene glycol excess distilled off. The molten reaction product is transferred

to a polycondensation vessel, mixed with 1.65 g (165 ppm) H_3PO_3 as sequestering agent and 1.27 g (127 ppm) cobalt acetate (corresponding to 30 ppm Co) and agitated for 10 to 15 minutes at 230°C. 0.27 g (27 ppm) potassium titanyloxalate (corresponding to 3.6 ppm Ti) is then added and the charge agitated under nitrogen at 240°C, during which ethylene glycol is distilled off under low vacuum. The internal pressure is then reduced to 1.13 mbar over an hour and the temperature of the melt then increased from 240 to 270°C. Over another half-hour, the temperature is raised to 280°C and agitation continued until a sample of the melt has a specific solution viscosity of 0.83, measured in a solution of 1 g of melt in 100 mL dichloroacetic acid at 25°C.

[0056] As an alternative and more conveniently, polycondensation can also be continued to a specified melt viscosity, if the melt viscosity that corresponds to a solution viscosity of 0.83 was determined in preliminary experiments.

[0057] The melt is cooled and processed in the usual manner to pellets with a diameter of 2 to 3 mm. The polyester so obtained has the following characteristics:

Content of carboxyl groups (mmol/kg): 12

Content of diethylene glycol (%): 0.5

Color indices: $L^* = 63.44$; $a^* = -0.62$; $b^* = 3.09$

[0058] The polyester so produced can be further condensed by solid condensation. For this purpose, the pellets produced above are heated in the usual manner during slow mixing in vacuum or under nitrogen for 17 hours to 220°C. A polyester with a specific viscosity of 1.014, as measured above, is obtained.

Examples 1b to 1l

[0059] The above example was repeated a number of times in the batchwise method described in example 1a (examples 1j to 1l) or similarly in a continuous operation (examples 1b to 1l), in which the amount of cobalt additive, the type and amount of sequestering agent, as well as the type and amount of titanium catalyst, were modified and, in some cases, a commercial optical brightener ([®]HOSTALUX KS from Hoechst AG) or a cross-linking agent (pentaerythritol) was additionally added. During melt polycondensation, different pressures and varied reaction times were used and the condensation time and temperature were varied in solid condensation.

[0060] The composition of the charges in the reaction condition, if varied, the color indices, as well as the achieved specific viscosity and content of carboxylic acid groups and diglycol in the polyester, are given in the following tables 1 and 2.

[0061] The abbreviations used in the table have the following meanings:

KTi = potassium titanyloxalate

Tiip = Isopropyl titanate

Co(ACO)₂·4 H₂O = cobalt acetate tetrahydrate

PO₃ = phosphorous acid

PO₄ = phosphoric acid

PPA = polyphosphoric acid

PHM = PHM ester

HLX = ®HOSTALUX KS

Penta = Pentaerythritol

SV = specific viscosity

[COOH] carboxyl terminal group concentration

DEG = concentration of diethylene glycol

[0062] All ppm data refer to the amount of polyester theoretically obtained in the charge. If the additive is a metal compound (for example, catalyst), the name of the compound abbreviation means that the ppm amount denotes the amount of compound, if the metal symbol is stated, the ppm amount denotes the amount of metal contained in the additive.

Table 1

| Example No. | Polycondensation catalyst | | Cobalt compound | | | Sequestering agent | | Additional additive | |
|-------------|--------------------------------|--------------|---------------------|--------------------|-----------------|--------------------|--------------------|---------------------|--------------|
| | Type | Amount (ppm) | Type | Amount (ppm) total | Amount (%) free | Type | Amount (ppm) total | Type | Amount (ppm) |
| 1b | KTi | 27 | Co(Ac) ₂ | 84 | 0 | PO3 | 150 | - | - |
| 1c | KTi | 27 | Co(Ac) ₂ | 84 | 0 | PO3 | 150 | HLUX | 10 |
| 1d | KTi | 27 | Co(Ac) ₂ | 127 | 0 | PO3 | 165 | HLUX | 10 |
| 1e | KTi | 27 | Co(Ac) ₂ | 127 | 0 | PO3 | 165 | Penta | 200 |
| 1f | KTi | 54 | Co(Ac) ₂ | 127 | 0 | PO3 | 165 | - | - |
| 1g | KTi | 54 | Co(Ac) ₂ | 169 | 0 | PO3 | 189 | - | - |
| 1h | KTi | 27 | Co(Ac) ₂ | 127 | 100 | PO3 | 121 | - | - |
| 1i | Sb ₂ O ₃ | 395 | - | - | - | PO3 | 121 | - | - |
| 1j | KTi | 45 | Co(Ac) ₂ | 135 | 10 | PO3 | 140 | Penta | 200 |
| 1k | KTi | 27 | Co(Ac) ₂ | 127 | 100 | PO3 | 121 | - | - |
| 1l | Sb ₂ O ₃ | 390 | - | - | - | PO3 | - | - | - |

Table 2

| Example No. | Melt condensation | | SV | (COOH) (mmol/kg) | DEG (%) | Color indices | | | Solid condensation | | SV |
|-------------|-------------------|------------|-------|------------------|---------|---------------|-------|-------|--------------------|-----------|-------|
| | Pressure (mbar) | Time (Min) | | | | L* | a* | b* | Time (h) | Temp (°C) | |
| 1b | 1.1 | - | 0.851 | 11 | 0.47 | 65.76 | -1.19 | 5.89 | 14 | 220 | 1.048 |
| 1c | 0.9 | - | 0.835 | 15 | 0.48 | 66.57 | -0.62 | 4.07 | 16 | 220 | 1.057 |
| 1d | 0.8 | - | 0.835 | 13 | 0.48 | 64.95 | 0.12 | 0.98 | 18.5 | 220 | 1.019 |
| 1e | 1.1 | - | 0.826 | 10 | 0.53 | 67.30 | 0.12 | 0.77 | 14 | 220 | 1.032 |
| 1f | 1.6 | - | 0.848 | 12 | 0.55 | 66.19 | -0.94 | 4.92 | 10.5 | 220 | 1.063 |
| 1g | 1.0 | - | 0.840 | 12 | 0.50 | 64.37 | 0.27 | -0.11 | 16 | 220 | 1.000 |
| 1h | 1.3 | - | 0.846 | 17 | 0.53 | 66.28 | -0.03 | 2.34 | 14 | 220 | 1.055 |
| 1i | 1.6 | - | 0.829 | 13 | 0.55 | 64.07 | -2.31 | 7.27 | 9.25 | 220 | 1.038 |
| 1j | 0.8 | 141 | 0.832 | 15 | 0.74 | 62.75 | 0.86 | 2.65 | 12 | 225 | 1.048 |
| 1k | 0.8 | 189 | 0.853 | 9 | 0.72 | 66.35 | -0.30 | -0.19 | 12 | 220 | 1.134 |
| 1l | 0.8 | 184 | 0.834 | 11 | 0.63 | 64.64 | -2.51 | 4.16 | 12 | 225 | 1.053 |

Example 2

[0063] The following practical example explains production of a polyester by means of a direct esterification:

[0064] An esterification reactor is fed with 8.29 kg of terephthalic acid, 0.124 kg of isophthalic acid and 4.0 kg of ethylene glycol and the mixture is heated during agitation under nitrogen as protective gas under a pressure of 3.2 bar, so that the split-off water is distilled.

[0065] When water cleavage is ended, the molten reaction product is transferred to a polycondensation vessel, mixed with 0.35 g (32 ppm) H_3PO_3 as sequestering agent and 1.47 g (135 ppm) cobalt acetate tetrahydrate (corresponds to 32 ppm Co). 0.49 g (45 ppm) potassium titanyl oxalate (corresponds to 6.1 ppm Ti) is then added and the charge agitated under nitrogen at 240°C, during which ethylene glycol is distilled off under low vacuum.

[0066] The internal pressure is then reduced to 1.13 mbar over an hour and the temperature of the melt raised from 240 to 270°C. Over another half-hour, the temperature is then raised to 280°C and agitation continued until a sample of the melt has a specific solution viscosity of 0.83, measured in a solution of 1 g of melt in 100 mL dichloroacetic acid at 25°C. The melt is cooled and processed in the usual manner to pellets with a diameter of 2 to 3 mm.

[0067] The polyester so obtained has the following characteristics:

Content of carboxyl groups (mmol/kg): 13

Content of diethylene glycol (%): 1.19

Color indices: $L^* = 63.6$; $a^* = 1.90$; $b^* = -1.5$

[0068] The polyester so produced can be further condensed by solid condensation. For this purpose, the pellets prepared above, during slow mixing, are

[0069] heated under nitrogen or in vacuum for 9.5 hours to 220°C. A polyester with a specific viscosity of 1.087, as measured above, is obtained.

[0070] In similar fashion, with the conditions apparent from Tables 3 and 4, additional polyesters can be produced. The products have the features apparent from Table 4.

Table 3

| Example No. | Polycondensation catalyst | | Cobalt compound | | | Sequestering agent | | Additive | |
|-------------|--------------------------------|--------------|---------------------|--------------|--------|--------------------------------|--------------|----------|--------------|
| | Type | Amount (ppm) | Type | Amount (ppm) | % free | Type | Amount (ppm) | Type | Amount (ppm) |
| 2b | Sb ₂ O ₃ | 298 | - | - | - | H ₃ PO ₃ | 32 | Penta | 200 |
| 2c | KTi | 45 | Co(Ac) ₂ | 84 | 100 | - | - | Penta | 200 |
| 2d | KTi | 45 | Co(Ac) ₂ | 135 | 25 | H ₃ PO ₃ | 32 | Penta | 200 |

Table 4

| Example No. | Melt condensation pressure (mbar) | SV | -COOH (mmol/kg) | DEG (%) | Color indices | | |
|-------------|-----------------------------------|-------|-----------------|---------|---------------|------|-----|
| | | | | | L* | a* | b* |
| 2b | 2.75 | 0.812 | 20 | 1.51 | 62.8 | -1.8 | 5.2 |
| 2c | 4.7 | 0.814 | 21 | 1.49 | 63.6 | 0.5 | 4.7 |
| 2d | 2.35 | 0.823 | 12 | 1.36 | 64.6 | 1.7 | 0.9 |

Claims

1. A heat-resistant, color-neutral, antimony-free polyester based on aromatic dicarboxylic acids and aliphatic diols, characterized by the fact that it is prepared by means of

- a)

- (i) esterification of aromatic dicarboxylic acids with aliphatic diols or
 - (ii) transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols in the presence of 20 to 120 ppm, in reference to the catalyst metal, of a transesterification catalyst, which is inactivated after conclusion of transesterification by addition of a sequestering agent, and

- b) subsequent polycondensation in the presence of a titanium compound as catalyst,

in which, after conclusion of esterification or transesterification,

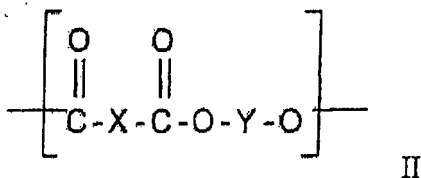
- 100% of the amount equivalent to the employed transesterification catalyst and
- 90 to 99% of the amount equivalent to the employed cobalt of phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives are added to the esterification or transesterification charge and then
- 20 to 80 ppm cobalt in the form of a cobalt compound

is added to the charge, and the polycondensation is run without the addition of antimony in the presence of 1 to 10 ppm titanium, which is added in the form of a titanium compound.

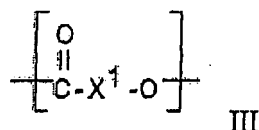
2. The polyester according to Claim 1, characterized by the fact that, in the unmatted state, among its color index components

- a* lies in the range from -3 to +3,
 - b* lies in the range from -6 to +6 and
 - L* lies in the range from 55 to 75.

3. The polyester according to Claim 1 or 2, characterized by the fact that it is antimony-free and contains 1 to 10 ppm titanium, 20 to 120 ppm of a transesterification catalyst metal in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, as well as 0 to 80 ppm cobalt, which is partially present in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, and optionally up to 50 ppm of an optical brightener.
4. The polyester according to at least one of the Claims 1 to 3, characterized by the fact that it is antimony-free and contains 2 to 8 ppm titanium, 50 to 90 ppm manganese (calculated as metal) in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, 20 to 40 ppm cobalt, which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives, and optionally up to 25 ppm of an optical brightener.
5. The polyester according to at least one of the Claims 1 to 5, characterized by the fact that, in the unmatted state, among its color index components
 - a* lies in the range from -2 to +2,
 - b* lies in the range from -3.5 to +3.5 and
 - L* lies in the range from 60 to 70.
6. The polyester according to at least one of the Claims 1 to 5, characterized by the fact that 90 to 99% of the cobalt is present in the form of catalytically inactive complexes of phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives.
7. The polyester according to at least one of the Claims 10 to 14, characterized by the fact that it contains 5 to 25 ppm of an optical brightener.
8. The polyester according to at least one of the Claims 1 to 7, characterized by the fact that its polymer chains are constructed from 80 to 100 mol% structural groups of formula II



and 20 to 0 mol% structural groups of formula III



in which

- X denotes more than 80 mol% aromatic groups with 5 to 16, preferably 6 to 12, carbon atoms and a maximum of 20 mol% aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,
- X¹ denotes the p-phenylene group,
- Y denotes at least 80 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a maximum of 20 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$, in which n is whole number from 1 to 40, in which n = 1 or 2 is preferred for fractions up to 20 mol%, and groups with n = 10 to 40 are preferably only present in fractions of less than 5 mol%.

9. The polyester according to at least one of the Claims 1 to 8, characterized by the fact that it consists of structural groups of formula II, in which

- X denotes up to 90 to 100 mol% p-phenylene groups, 0 to 7 mol% m-phenylene groups and 0 to 5 mol% aliphatic groups of 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and
- Y denotes at least 90 mol% alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylenecycloalkane groups with 6 to 10 carbon atoms and a maximum of 10 mol% straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$, in which n stands for the numbers 1 or 2.

10. The polyester according to at least one of the Claims 1 to 9, characterized by the fact that it consists of structural groups of formula II, in which X denotes up to 93 to 99 mol% p-phenylene groups and 1 to 7 mol% m-phenylene groups.
11. The polyester according to at least one of the Claims 1 to 10, characterized by the fact that the catalytically inactive complexes of manganese and cobalt are complexes with phosphorous acid or its ester.
12. The polyester according to at least one of the Claims 1 to 11, characterized by the fact that it optionally contains up to 1000 ppm crosslinking structural groups.

